44

# TOPOTACTIC TRANSFORMATIONS IN IRON OXIDES AND OXYHYDROXIDES*

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Plate VIII (A and B)

**ABSTRACT.** This paper records an investigation of the structures and chemical relations of iron oxides, hydroxides and oxyhydroxides. In the course of the work structural relations were also found between them which exemplified the new concept of topotaxy or change of composition of crystals occurring without any large discontinuity of structures. Starting with $Fe(OH)_2$ whose structure is built up of hexagonal close-packed hydroxyl layers, it is seen that when it decomposes into FeO there is an oriented relationship between the two phases. The [001] of $Fe(OH)_2$ becomes the [111] of cubic FeO and [110] of the former becomes [110] of the latter. Again, when $Fe(OH)_2$ is oxidised by strong $H_2O_2$ or $(NH_4)_2S_2O_8$ solution to $\delta$ FeO.OH, the arrangement of the close-packed layers changes from AcB to $A\frac{1}{2}cB\frac{1}{2}cA$, the directions of the axes remaining the same. As it was not possible to get any single crystals of green rusts, direct evidences about the oriented relationship between them and their transformation products could not be found. But the proposed structure for the green rusts definitely speaks in favour of the oriented relationships. The transformations of $\gamma$-FeO.OH to $\gamma$-$Fe_2O_3$ and then to $\alpha$-$Fe_2O_3$ have been studied in great detail. It was found that the [100], [010] and [001] axes of $\gamma$-FeO.OH become [001], [110] and [110] of $\gamma$-$Fe_2O_3$ after transformation. In the second transition from $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$, crystals of the latter grow with their [001] axes parallel to [111] of $\gamma$-$Fe_2O_3$ and their [110] directions being parallel to [110] of $\gamma$-$Fe_2O_3$. The same sort of oriented relationship as in between $\gamma$-$Fe_2O_3$ and $\alpha$-$Fe_2O_3$ was found in the transformation of $Fe_3O_4$ to $\alpha$-$Fe_2O_3$. Several forms of $\gamma$-$Fe_2O_3$ prepared by various methods have also been studied by X-rays. The transformation of rhombohedral $FeCO_3$ to cubic FeO and $Fe_3O_4$ has also been found to have oriented relationship. The similarity of the structures of $FeCO_3$ and FeO suggested that the triad axis of $FeCO_3$ would be parallel to one of the triad axes of FeO and that the three diad axes of both phases were interchanged, FeO and $Fe_3O_4$ having parallel orientation to each other. The transformation of $\beta$-FeO.OH to $\alpha$-$Fe_2O_3$ could not be explained in terms of oriented relationship. From the similarity of the powder patterns and also the comparison of intensities of the diffraction lines, it is thought that $\beta$-FeO.OH has a structure similar to Hollandite mineral ($\alpha$-$MnO_2$).

## INTRODUCTION

Up to the present time physico-chemical studies have shown the existence of three forms of iron oxyhydroxides referred to as $\alpha$, $\beta$ and $\gamma$-$Fe_2O_3$, $H_2O$ or FeO.OH.

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Of the anhydrous oxides of iron, $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$ and $Fe_3O_4$ can be obtained by dehydrating some of the oxyhydroxides (FeO.OH), by direct precipitation or by oxidation of $Fe(OH)_2$ with different types of oxidising agents. The remaining anhydrous oxide, FeO, may be obtained by decomposing $Fe(OH)_2$ or some organic ferrous salts in vacuo or in an inert atmosphere. Most of these hydrous and anhydrous oxides of iron can be found as natural minerals. Together with the study of various physical and chemical properties of these compounds, a number of methods have been found for preparing them synthetically. Welo and Baudisch (1925, 1933, 1935) reviewed all the work done on the iron oxides and oxyhydroxides up to that time and tried to draw up a general relationship between the different iron compounds. However, they themselves expressed doubts about the existence of some members in the iron oxide-oxyhydroxide system and also about the modes of transformation between the compounds. Although various methods of preparing the different oxides and oxyhydroxides and also how one can be obtained from the other are known, the structural inter-relationships among these compounds are quite unknown.

The structures of most of the oxides and oxyhydroxides of iron are built up of close-packed oxy/hydroxyl layers. It seems possible that when one form of iron oxides or oxyhydroxides transforms into another, the change may be effected simply by removing or adding close-packed oxy/hydroxyl layers from or to the original structures. Thus one might expect to find an oriented relationship between the original and transformed products. Such a relationship, which is not limited to any particular type of crystal, was observed by Goldsztanb (1931, 1935) in the transformation of $\alpha$-FeO.OH to $\alpha$-$Fe_2O_3$. This sort of relationship occurs frequently in metals and also in inorganic compounds. A striking example of this oriented relationship can be found in the case of cubic and hexagonal metallic cobalt crystals. There the basal hexagonal face becomes one of the {111} faces of the face-centred cubic form. Similarly, in the transformation between $\alpha$ and $\gamma$-iron, the {110} faces of the body-centred form becomes the close-packed {111} faces of the face-centred cubic form. All these changes mean that the main determining elements of the lattice do not change and the other elements only move from one symmetrical position to another in substantially the same cell. The minimum disturbances caused when the hydroxyl ions are removed as water molecules also suggest that the evidence of oriented relationship among the oxides and oxyhydroxides of iron may be found.

The best method of studying these oriented transformations is to make X-ray investigations on single crystals of different compounds before and after the transformation and also during it, if possible. If an oriented relationship exists, the diffraction photographs taken both before and after the transformation will show some common directions. When single crystals are not available, the powder diffraction method can provide indirect evidence. Sometimes, accord-

ing to the nature of transformation, a multiplicity of the reflections may correspond to a single direction from the original crystal. In this case, the similarities between the structure of the two phases may throw some light on any possible inter-relationship.

This sort of inter-relationship can be explained in terms of topotaxy, a term proposed by Gorter to denote the transformation from one crystalline phase to another, where there are definite oriented relationships between the axes of the original and transformed crystals. In general, the topotactic change consists of two parts, geometrical and chemical. The geometrical part classifies the way in which one lattice can be transformed into another while retaining the original network of the structure. The chemical part, on the other hand, accounts for the possibility of replacing one kind of atom by another and also the increase or lowering the total number of atoms per unit of lattice. True topotactic changes involve more than internal rearrangements of atoms along with the substitution, removal or addition of atoms to the original structure. In general, topotactic changes involving the loss or gain of atoms will leave the main symmetry directions of the crystals unchanged. But it also seems possible that an asymmetrical crystals may, by the loss of its atoms, transform into a form of higher symmetry. Further topotactic changes may occur on the newly formed crystals.

Thus with the aim of establishing what structural relationships exist between the different phases, most of iron oxides and oxyhydroxides and their transformations from one to the other have been studied in great detail. The results of the investigations are given in the next section.

## EXPERIMENTAL RESULTS

### (a) *Ferrous hydroxide* ($Fe(OH)_2$)

Thesn ow-white precipitate of $Fe(OH)_2$ which is obtained when an alkali is added to a ferrous salt solution, turns greenish as soon as it comes in contact with air. To show the true colour of $Fe(OH)_2$ precipitate, it is necessary to boil both the alkali and salt solution before mixing in order to eliminate the dissolved oxygen and the precipitation must be carried out in an inert atmosphere. Natta and Casazza (1928) from the powder diffraction photograph determined the structure of $Fe(OH)_2$. They found it to be hexagonal with one formula unit in the unit cell of axial parameters $a = 3.24$ Å and $c = 4.47$ Å. Thes tructure is built of two hexagonal close-packed $OH'$ layers having Fe in the octahedral position in between them. The atomic coordinates are one Fe at (0,0,0) and two OH at $\pm(2/3, 1/3, Z)$ with $Z = 0.26$. It is to be noted here that the $OH'$ layer has $Fe^{++}$ on one side of it, whereas on the other side it is bound to another $OH'$ layer by hydroxyl bonds.

Though it is thought that $Fe(OH)_2$ is very unstable at ordinary temperature and in contact with air, recent work by Shipko and Douglas (1956) had shown

that pure $Fe(OH)_2$, in contact with a solution of potassium chloride or excess of hydroxyl ion with complete exclusion of oxygen, was stable for a period of six months. Moreover, Gayer and Woonter (1957) reported from their chemical analysis that the green precipitate, observed at the initial stage of the oxidation of white $Fe(OH)_2$, no traces of ferric ions were found. Our (1960) work also showed that even when 20% of $Fe^{++}$ ion in $Fe(OH)_2$ was oxidised to $Fe^{+++}$, there was no change in the structure of $Fe(OH)_2$.

When the white precipitate of $Fe(OH)_2$ is washed with oxygen free water and then heated to dryness it decomposes to FeO, some $Fe_3O_4$ also being formed at the same time. Recently, Goodman (1958) has shown from electron microscope and electron diffraction study of single crystal of $Mg(OH)_2$ that on dehydration of $Mg(OH)_2$ to MgO there is an oriented relationship between the two phases: the [001] of the hexagonal $Mg(OH)_2$ crystal transforms into [111] of the cubic MgO and the [110] of $Mg(OH)_2$ becomes [110] of MgO. As $Fe(OH)_2$ is very unstable, it was not possible to study the oriented relationship between $Fe(OH)_2$ and FeO using single crystal. From the fact that both $Mg(OH)_2$ and $Fe(OH)_2$ have the same structure ($CdI_2$ type) and also from the similarity between the MgO and FeO structure (NaCl type), it seems reasonable to think that in the transformation of $Fe(OH)_2 \rightarrow FeO$, the same type of oriented relationship occurs. Fig. 1 shows how two hydroxyl layers in $Fe(OH)_2$ could combine together to form a single

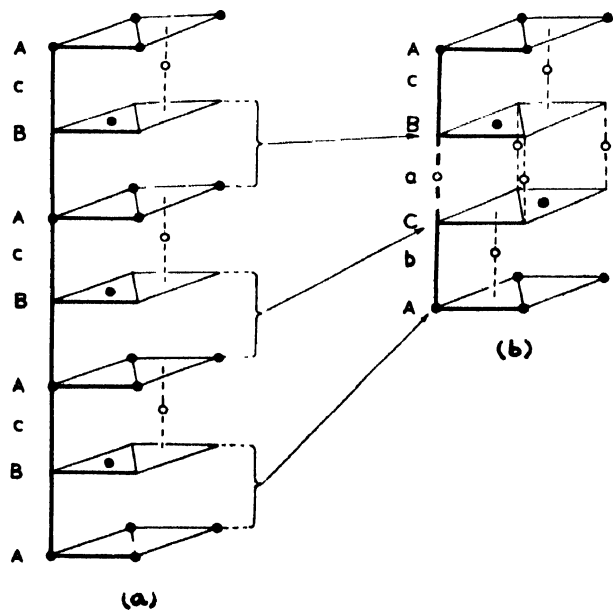



Fig. 1 Transformation of $Fe(OH)_2 \rightarrow FeO$.
(a) The arrangement of hydroxyl layers along [001] of $Fe(OH)_2$
(b) The arrangement of oxygen layers along [111] of FeO.

layer of oxygen in FeO. The oriented relationship which occurs between FeO and $Fe_3O_4$ has been discussed later on.

(b) *Delta ferric oxyhydroxide* ($\delta$-FeO.OH)

$Fe(OH)_2$ in alkaline solution, when oxidised by air or oxygen, transforms into $\alpha$-FeO.OH. The possibility of oriented relationship between $Fe(OH)_2$ and $\alpha$-FeO.OH has been reported by Francombe and Rooksby (1959).

Glemser and Gwinner (1939) reported that $Fe(OH)_2$, when oxidised by $H_2O_2$ or $(NH_4)_2S_2O_8$ in excess, transformed into a ferromagnetic compound, which they called $\delta$-$Fe_2O_3$. The X-ray photograph of this $\delta$-$Fe_2O_3$ was interpreted by them in terms of a hexagonal cell with axial parameters $a$ = 5.09 A and $c$ = 4.41 A. This particular compound was studied by us in great detail and found not to be an anhydrous oxide of iron but an oxyhydroxide (FeO.OH). Moreover, the X-ray diffraction photograph was indexed in terms of a smaller hexagonal cell with $a = 2.941 \pm 0.005$ Å and $c = 4.49 \pm 0.01$ A (Bernal, Dasgupta and Mackay, 1959).

Though stable at room temperature, $\delta$-FeO.OH could not be obtained in the form of a single crystal. Hydrothermal treatment was attempted but it was found that when powdered $\delta$-FeO.OH was heated in a bomb at 100°C, it was converted into $\alpha$-$Fe_2O_3$. From the similarity of the powder pattern and axial parameters of $\delta$-FeO.OH and $Fe(OH)_2$ and also from the fact that the pattern of $\delta$-FeO.OH could be obtained from that of $\alpha$-$Fe_2O_3$ by choosing lines with l indices divisible by 3, it seems reasonable that the structure of $\delta$-FeO.OH is intermediate between those of $Fe(OH)_2$ and $\alpha$-$Fe_2O_3$. It should be pointed out here that in $Fe(OH)_2$, OH layers have Fe on one side of it, whereas on the other side they are connected to another OH layer by hydroxyl bonds. But in $\alpha$-$FO_2O_3$, the hexagonal close-packed oxygen layers have Fe, in the octahedral sites, on both the sides. The striking feature of the powder pattern of $\delta$-FeO.OH is the very weak (often absent) (001) reflection. This suggests that iron must be in the octahedral position on both sides of the close packed O′/OH′ layers. The density of $\delta$-FeO.OH allows only one formula unit in the unit cell. The number of iron in the unit cell is thus one. To satisfy the condition for the 001 reflection, half of this iron should occupy the octahedral position on side of the closepacked layer, the other half being placed at the octahedral side on the other side of the layer. Fig. 2. shows the probable structure of $\delta$-FeOH compared to that of $Fe(OH)_2$.

Feitknecht (1943) observed a similar type of structure for Cd(OH)F, where $Cd^{++}$ ions are distributed equally between two octahedral sites between two hexagonal close-packed layers of mixed OH′ and F′ ions. However, in the case of $\delta$-FeO.OH a better agreement between the observed and calculated intensities was found when 78% of the total iron was placed equally at the two octahedral sites (0,0,0; 0, 0, $\frac{1}{2}$) and the remaining part of iron in the four tetrahedral positions at $\pm$(1/3, 2/3, 1/8) and $\pm$(2/3, 1/3, 3/8).

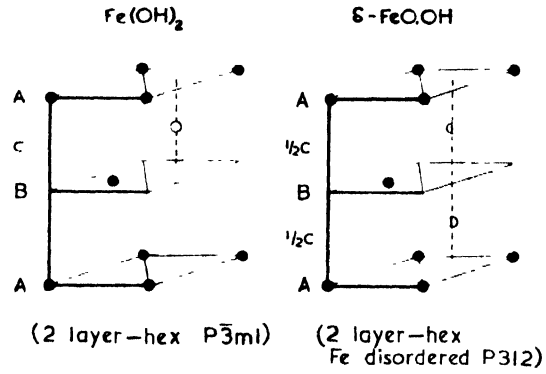



Fig. 2 Comparison of $Fe(OH)_2$ and δ-FeO.OH structure, the layers being shown along [001] axes.

(c) *The basic ferrous complexes*

When alkali insufficient to allow the complete precipitation of $Fe(OH)_2$ is added to ferrous salt solution a series of unstable complexes of ferrous salts are formed. Keller (1948) reported three basic chlorides obtained by partial precipitation from $FeCl_2$ with various concentrations of alkali. The basic complexes and their transformation on oxidation or dehydration have been studied by (1959). Of these complexes two are from $FeCl_2$ solution and the other from $FeSO_4$ solutions, are of great importance as they, on oxidation transform into γ-FeO.OH. These two complexes have been referred as green rust I and II respectively. The green rust I was found to belong to the hexagonal crystal system but the axial parameters varies for different preparations as follows :

(i) $a = 3.198 \pm 0.005$ Å, $c = 24.21 \pm 0.01$ Å from $FeCl_2$

(ii) $a = 3.23 \pm 0.01$ Å, $c = 22.50 \pm 0.01$ Å from $FeSO_4$

(iii) $a = 3.18 \pm 0.01$ Å, $c = 22.80 \pm 0.01$ Å from $FeBr_2$.

During oxidation green rust I, prepared from $FeSO_4$ solution, passed through another phase before being finally converted into γ-FeO.OH. This phase, termed as green rust II, also belongs to hexagonal crystal system with $a = 3.17 \pm 0.01$ Å and $c = 10.90 \pm 0.01$ Å.

Due to the instability of the green rusts it was not possible to make a complete study of their structures. However, from the dimensions of their axial lengths and the nature of the layer structures of almost all the oxides and hydroxides of iron some speculations can be made as to their structures in terms of the packing of equal spheres, if the following assumptions are made.

(i) Hexagonal layers of anions (O″ or OH″) are stacked so that regular tetrahedra fill the space. The layer distance is thus $0.817a$ where $a$ is the diameter of the anion.

(ii) There will be empty tetrahedral and octahedral sites available for cations. There is no great distortion of the structure in filling these and the consideration is restricted only to the octahedral holes.

(iii) The sharing of faces by co-ordination octahedra (or tetrahedra) round the cation is rejected (Pauling's rule).

(iv) The compounds are all stoichiometric.

There are then only the following number of possibilities of stacking, where A, B, C denote the anions at (0, 0, Z); (1/3, 2/3, Z) and *a*, *b*, *c* denote the anions with the same co-ordinates.

(a) 2 *layers* : Composition $AO_2$; sequence of layers AcB—A ($c$ = 1.633a hexagonal)

(b) 3 *layers* : (i) composition AO; sequence of layers AcBaCbA (cubic $a$ = 1.414a), (ii) composition $A_2O_3$, sequence of layers, AcBbC A($c$ = 2.45a hexagonal), (iii) composition $AO_3$, sequence of layers AcB C A ($c$ = 2.45$a$ hexagonal).

(*c*) 4 *layers*: composition $A_2O_4$, sequence of layers AcB—AbC A or A—BcAbC A ($c$ = 3.27$a$ hexagonal).

(d) 6 *layers* : composition $AO_2$ sequence of layers AcB-cbA BaC—A. ($c$ = 4.90a, rhombohedral).

(*e*) 9 *layers* : composition $A_2O_3$; sequence of layers AcBaC BaCbA—CbAcB—A (rhombohedral); composition $AO_3$; sequence of layers AcB C—BaC—BaC A—CbA A or A—B CaB—C AbC—BcA ($c$ = 7.35$a$, rhombohedral).

From the above considerations, it appears that as a first approximation the green rust I has the 9-layers rhombohedral structure ($c/a$ = 7.2 observed) and green rust II has a 4-layers structure ($c/a$) = 3.4 observed). Fig. 3 shows the possible structures of green rust I and II based on these assumptions.

(d) *α and γ-Ferric oxyhydroxides* (*α and γ*-FeO.OH)

These two oxyhydroxides of iron occur as natural mineral Goethite and Lepidiscite respectively. Synthetically, Goethite (α-FeO.OH) can be prepared by oxidising the green rusts. There are also other methods of preparation of these two oxyhydroxides synthetically.

α-FeO.OH transforms into α-$Fe_2O_3$ on dehydration. Goldsztaub (1931), while studying the transformation of single crystals of α-FeO.OH into α-$Fe_2O_3$, found an oriented relationship between them. He showed that the [100], [010] and [001] axes of the orthorhombic cell of α-FeO.OH transformed into [111], [110] and [112] axes respectively of the rhombohedral cell of α-$Fe_2O_3$.

γ-FeO.OH, on the other hand, transforms into γ-$Fe_2O_3$ dehydration and then to α-$Fe_2O_3$ on further heating. The transformation of γ-FeO.OH→γ-$Fe_2O_3$→α-$Fe_2O_3$ was studied by us (Bernal, Dasgupta and Mackay, 1957) using single

crystals of $\gamma$-FeO.OH. It was found that $\gamma$-$Fe_2O_3$ crystals are formed with their [001], [110] and [110] axes parallel to [100] [010] and [001] axes respectively of

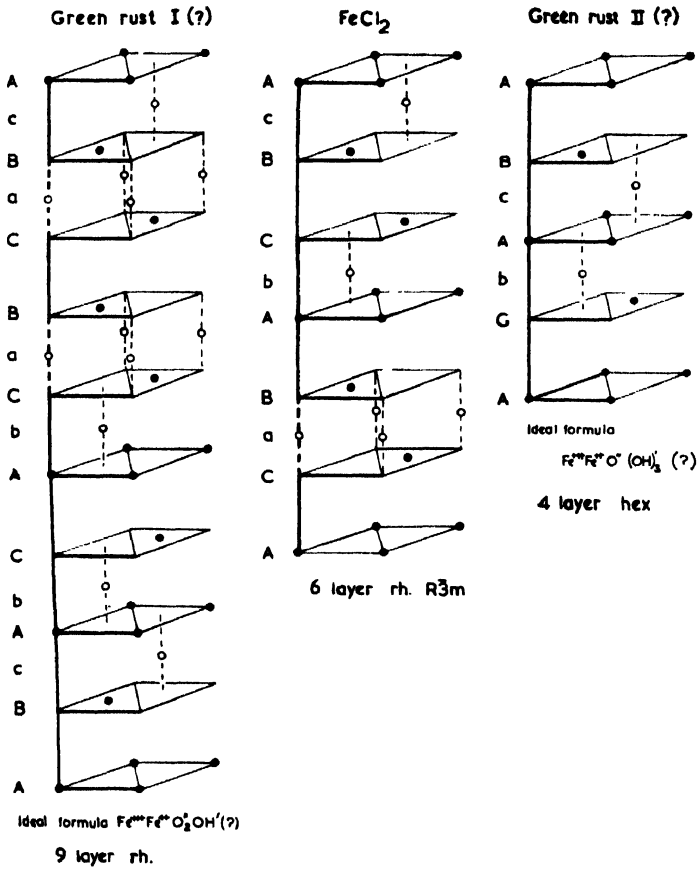
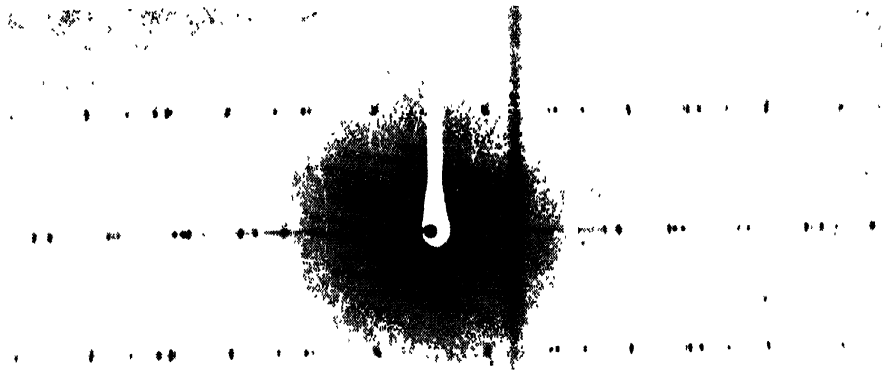



Fig. 3 Proposed structures of green rust I & II.

$\gamma$-FeO.OH. That the [100] of $\gamma$-FeO.OH is parallel to one of the cubic axes [001] of $\gamma$-$Fe_2O_3$ could be seen from the X-ray photograph (Plate VIIIA, Fig. 4(a)(b). In the second transition from $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$, crystals of the latter grow with their [001] axes parallel to [111] direction of $\alpha$-$Fe_2O_3$ and their [110] directions being parallel to the [110] directions of $\alpha$-$Fe_2O_3$ Fig. 6.

The mechanism of the transformation can be explained as follows. Fig. 7 shows the similarity between $\gamma$-FeO.OH and $\gamma$-$Fe_2O_3$ (spinel type) structures. The transition would require the removal of half of the hydroxyl group together with the hydrogen in the adjoining hydroxyl sheet, as water molecules. This is followed closing up of the (010) layers from 12.57 Å to 8.85 Å, that is, by 30% or 1.86 Å per layer in the [010] direction of $\gamma$-FeO.OH. There is also a shift of half an



(b)

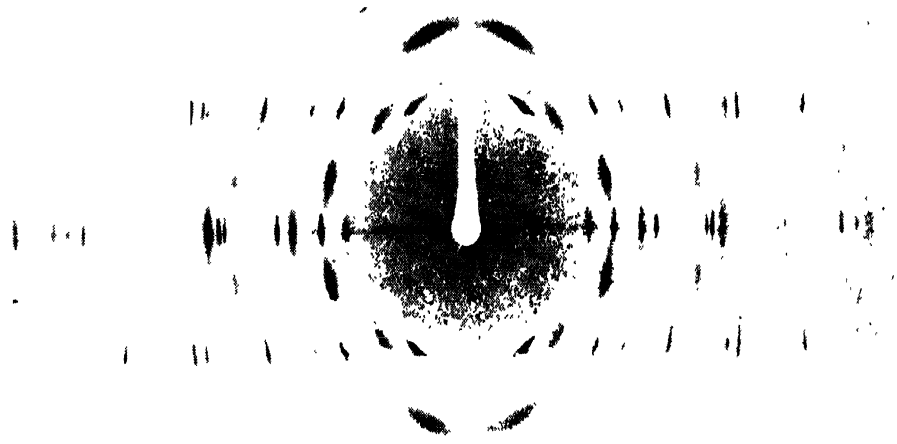


Fig. 4(a) Single crystal X-ray rotation photograph of $\gamma$-FeO taken along [100].

Fig. 4(b) Rotation photograph of a single crystal of $\gamma$-FeO.OH heated at 250°C for 3 hrs, showing the transformation $\gamma$-FeO.OH $\rightarrow$ $\gamma$-$Fe_2O_3$. The sharp spots correspond to unchanged $\gamma$-FeO.OH and the diffuse spots to $\gamma$-$Fe_2O_3$. The photograph was taken along the [100] axis of $\gamma$-Fe.OH and that corresponds to [001] axis of $\gamma$-$Fe_2O_3$.

(c)

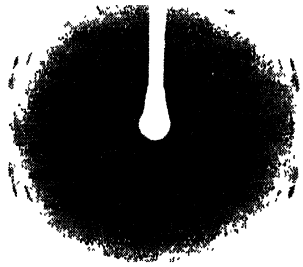


Fig. 4(c) Rotation photograph of single crystal of $\gamma$-$FeO.OH$ heated to 250°C for 20 hrs showing the transformation of $\gamma$-$Fe_2O_3$ $\alpha$-$Fe_2O_3$. The sharp spots are due to $\alpha$-$Fe_2O_3$ and the diffuse spots are due to $\gamma$-$Fe_2O_3$.

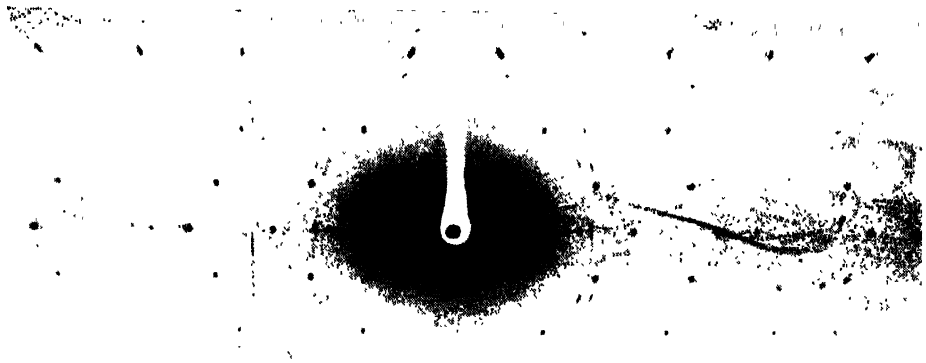


Fig. 5. Single crystal X-ray rotation photograph of $Fe_3O_4$ heated to 600°C for 26 hrs. taken along [100] of $Fe_3O_4$. The sharp spots are due to $Fe_3O_4$, while the weaker spots are due to $\gamma$-$Fe_2O_3$.

oxygen ion width (1.94 Å) in the [100] direction. The resulting strain due to the shift may explain the disorder in the $\gamma$-$Fe_2O_3$ crystal (diffuseness of the spots). From the fact that the $\alpha$-$Fe_2O_3$ crystals are oriented with respect to those of $\gamma$-$Fe_2O_3$ and not to those of $\gamma$-FeO.OH, it seems reasonable to think that the formation of $\alpha$-$Fe_2O_3$ is subsequent to that of $\gamma$-$Fe_2O_3$. This transformation does not involve any loss or gain of material but only a restacking of close-packed oxygen atoms (cubic to hexagonal) on the {111} faces of $\gamma$-$Fe_2O_3$ (Fig. 6).

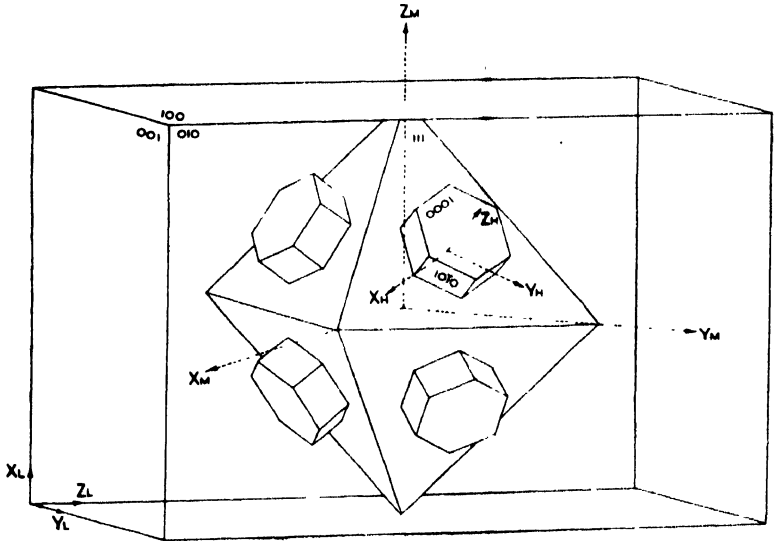



Fig. 6 Epitaxial relationship in the transformation $\gamma$-FeO.OH $\rightarrow$ $\gamma$-$Fe_2O_3$ $\rightarrow$ $\alpha$-$Fe_2O_3$.
Lepidocrocite Maghemite Haematite

(c) *Magnetite* ($Fe_3O_4$) *and Maghemite* ($\gamma$-$Fe_2O_3$)

The most important ferrite, Magnetite ($Fe_3O_4$), which may be written as $FeO.Fe_2O_3$, is the only certain oxide intermediate between ferrous and ferric oxides. Magnetite was known from very early ages to be one of the few ferromagnetic compounds as natural mineral. Magnetite which is cubic (face-centred) transforms into $\gamma$-$Fe_2O_3$ (cubic) on oxidation. $\gamma$-$Fe_2O_3$, on further heating, transforms into $\alpha$-$Fe_2O_3$, (hexagonal). The transition of $Fe_3O_4 \rightarrow \gamma Fe_2O_3 \rightarrow \alpha Fe_2O_3$ brought up by heating magnetite in air has been studied by several workers. It was found that synthetic magnetite transformed more easily into $\gamma$-$Fe_2O_3$ than the natural magnetite. While oxidising synthetic magnetite, it was found that there are four forms of $\gamma$-$Fe_2O_3$. Three of them belong to the cubic system, while the other belong to the tetragonal system (Bernal, Dasgupta and Mackay, 1959; Van Oosterhout and Rooymans, 1958). The oxidation of $Fe_3O_4$ on heating has received considerable attention largely because of the difference in the behaviour of the natural and synthetic $Fe_3O_4$. Experimental

works of Schmidt and Vermaas (1955), Lepp (1957) and of many others showed that synthetic $Fe_3O_4$ oxidised first to $\gamma$—$Fe_2O_3$ and then to $\alpha$-$Fe_2O_3$, whereas natural $Fe_3O_4$ oxidised only to $\alpha$-$Fe_2O_3$ usually at a high temperature. Our X-ray study on the natural single crystal of $Fe_3O_4$ also confirmed this observation, Plate VIIIB, Fig. 5. The early workers found, on oxidation of $Fe_3O_4$ to $\gamma$-$Fe_2O_3$, that some extra lines appeared in the X-ray photographs, the general pattern remaining the same. It was found that those extra lines could be accounted for if $\gamma$-$Fe_2O_3$ had a primitive cell ($Fe_3O_4$ is face-centred cubic) of the approximate dimensions of $Fe_3O_4$. In recent years, various workers have expressed doubts about the structure of $\gamma$-$Fe_2O_3$, which was proposed by Thewlis (1931). Hagg (1953) from his X-ray diffraction study of $\gamma$-$Fe_2O_3$ concluded that the changes in the intensities of the diffraction lines and also in the density of $\gamma$-$Fe_2O_3$, from those of $Fe_3O_4$, were produced by the vacant sites in the iron atom lattice in the spinel phase rather than by the addition of oxygen. The suggested structure for $\gamma$-$Fe_2O_3$ was a defect spinel with cation vacancies in an oxygen ion frame work. Hence, when $Fe_3O_4$ is written as $Fe_8^{++}\ Fe_{16}^{+++}\ O_{32}^{--}$, $\gamma$-$Fe_2O_3$ can be written as $Fe^{+++}_{21\cdot33}\ \square_{2\cdot67}\ O_{32}^{--}$ where $\square_{2\cdot67}$ denotes cation vacancies. Verwey (1935) also suggested a similar structure where the vacancies were preferentially located at the octahedral sites

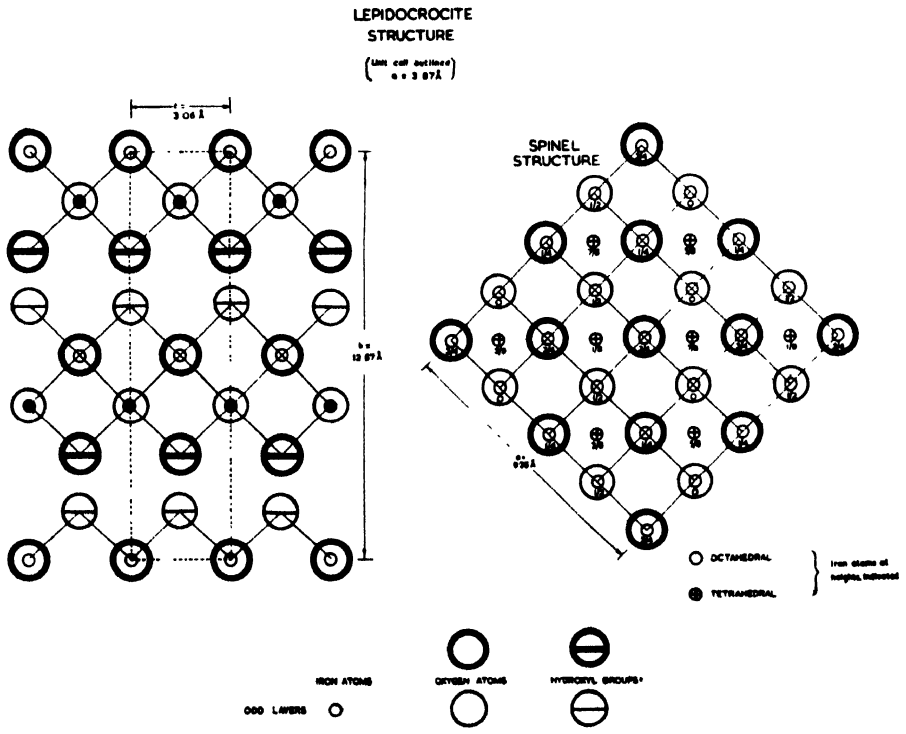



Fig. 7 Similarity of the $\gamma$-FeO.OH and $\gamma$-$Fe_2O_3$ (spinel) structures.

for Fe. This was supported by Henry and Boehm (1955) from their measurements of magnetic moment and also by Ferguson and Hass (1958) from their neutron diffraction study of $\gamma$-$Fe_2O_3$.

Since 1935, it has been generally accepted that $\gamma$-$Fe_2O_3$ is cubic with $10\frac{2}{3}$ molecules of $\gamma$-$Fe_2O_3$ in the unit cell. Van Oosterhout and Rooymans (1958) have shown that in $\gamma$-$Fe_2O_3$, prepared by decomposing ferrous oxalate dihydrate in an atmosphere of steam and nitrogen followed by an oxidation at 250°C, some extralines appeared in the x-ray photographs. It has been possible for them to assign indices to all these extra lines using a tetragonal cell having $c = 3a$ with $a$ same as that of the cubic cell. The new cell provides 32 molecules of $\gamma$-$Fe_2O_3$ instead of $10\frac{2}{3}$ in the cubic cell. It is seen that the structure of $\gamma$-$Fe_2O_3$ can be obtained from that of $Fe_3O_4$, when there is deficiency of Fe atoms in the octahedral sites of $Fe_3O_4$ structure. The relationship between $Fe_3O_4$ (or $\gamma$-$Fe_2O_3$)

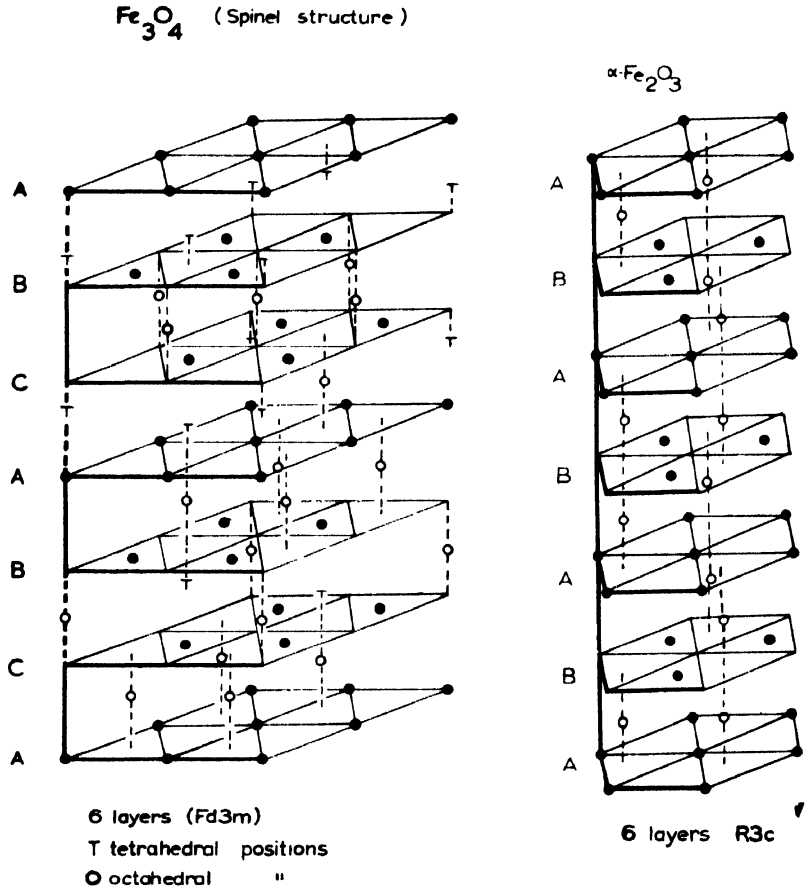



Fig. 8. Structural relationship between $Fe_3O_4$ and $\alpha$-$Fe_2O_3$ along their [111] and [001] axes respectively.

and $\alpha-Fe_2O_3$ structures has already been explained earlier and is shown diagramatically in Fig. 8.

(f) *Siderite or $FeCO_3$.*

Though $FeCO_3$ does not fall in the iron oxide and oxyhydroxide series, yet it has been included in the present paper as it decompases into FeO and $Fe_3O_4$ when heated at high temperature.

Single crystal of $FeCO_3$ was heated in a scaled tube to 550°C. At that temperature it was not magnetic but on cooling it becomes highly magnetic. Though this magnetism was accompanied by a change of colour, the crystal retained its original sharp edged rhombohedral form. The faces of the crystal appeared to be very rough when viewed with a high power microscope. An X-ray photograph taken with the heated crystal rotating along the apparent [110] axis shows it to be transformed into FeO and $Fe_3O_4$, both of them having an oriented relationship with the original crystal. From the measurement of the X-ray photograph, it was seen that there was no unchanged $FeCO_3$ or Fe. The indices of the spots along the zero layer line shows that the cubic phases (FeO and $Fe_3O_4$) are oriented parallel to each other. The diad axis of the $FeCO_3$ crystal becomes one of the diad axes of FeO and $Fe_3O_4$. The oriented relationship between FeO and $Fe_3O_4$ can be easily understood from the similarity of their structures. (Fig. 9).

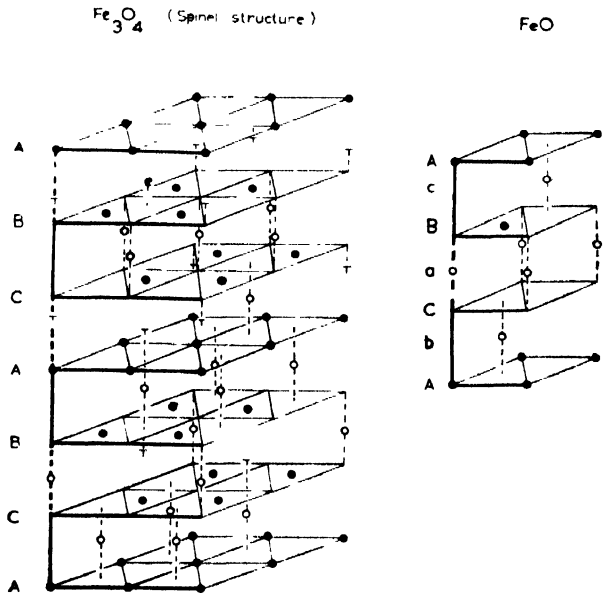



Fig. 9. Similarities between FeO and $Fe_3O_4$ structures showing the close-packed oxygen layers along the [111] directions.

The structure of $FeCO_3$ (rhombohedral), which is shown in Fig. 10, is not very different from those of NaCl or FeO. The FeO lattice compressed along [111]

axis would flatten out to become rhombohedral and make room for disc-shaped $CO_3$ ions in place of spherical O ions. So, it appears that FeO must derive from $FeCO_3$ simply by expulsion of $CO_2$ and change of angles between the sheet of atoms from 72° to 90°. The similarity also suggests that the triad axis of $FeCO_3$ will be parallel to one of the triad axes of the cubic crystal and that the three diad axes of both phases are interchanged. It is most remarkable that in spite of the loss of more than half of the oxygen atoms from the structure, the orientation is still preserved.

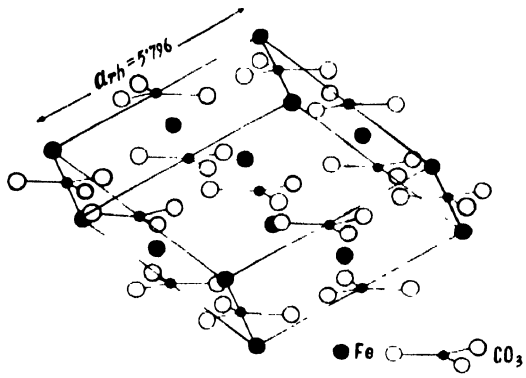



Fig. 10. structure of $FeCO_3$.

(g) *β-Ferric oxyhydroxide (β-FeO.OH)*

Weiser and Milligan (1935) reported this oxyhydroxide of iron. They found that when $FeCl_3$ was hydrolysed at 95°C for 6 hrs. the resultant brown precipitate was quite different from any of the existing oxides or oxyhydroxides of iron. From their dehydration isobar study, they concluded that it was a monohydrate of iron oxide ($Fe_2O_3$, $H_2O$ or FeO.OH). In the present study it was found that not only $FeCl_3$, but $FeF_3$ and also any other ferric salts in presence of $Cl'$ or $F'$ ions gave β-FeO.OH on hydrolysis. Kratky and Nowotny (1938) tried to index all the lines of the powder diffraction pattern of β-FeO.OH in terms of an orthorhombic cell with $a = 10.46$ Å, $b = 10.24$ Å and $c = 2.34$ Å. During the present investigation, it was found that all the lines in the powder photograph could be indexed in terms of a tetragonal cell with $a = 10.48 \pm 0.01$ Å and $c = 3.023 \pm 0.005$ Å. It will be worthwhile to mention here that no close pairs, such as (200, 020), (400, 040) where observed which could distinguish β-FeO.OH, as belonging to the orthorhombic crystal class.

As it was not possible to obtain any single crystals of β - FeO.OH, no detailed structure analysis could be carried out. Recently, Bystrom and Brystrom (1950) have determined the structure of the mineral hollandite and the related manganese oxide minerals. α-$MnO_2$ is tetragonal with $a = 9.8$ Å and $c = 2.86$ Å and Hollandite has a pseudotetragonal cell with $a = 9.96 \pm 0.05$ Å and $c = 2.86 \pm 0.01$ Å. The systematic absences in the case of hollandite are

the reflections with $h+k+l \neq 2n$. From the similarity of the powder pattern, axial lengths and the conditions for reflection (for $\beta$-FeO.OH, $h+k+l \neq 2n$), it seems that the two structures are similar. Fig. 11 shows the structure of Hollandite projected on (001). It can be seen that the metal ions are at the centre of the $MO_6$ octahedra and there are open channels parallel to $c$ axis. In the case of Hollandite, $Ba^{++}$ ions (its diameter being greater than the length of $c$ axis) are distributed along these channels statistically. From the fact that the percentages of $Cl^-$ or $F^-$ ions, which are essential or the formation of $\beta$-FeO.OH, are not constant in $\beta$-FeO.OH, it is highly probable that in case of $\beta$-FeO.OH, also $Cl'$ or $F'$ ions enter the structure but are not present stoichiometrically. It appears that the $Fe^{+++}$ ions, in the case of $\beta$-FeO.OH, should be at the centre of $Fe(O, OH)_6$ octahedra whereas the $Cl'$ or $F'$ ions are distributed statistically along the channel parallel to the $c$ axis.

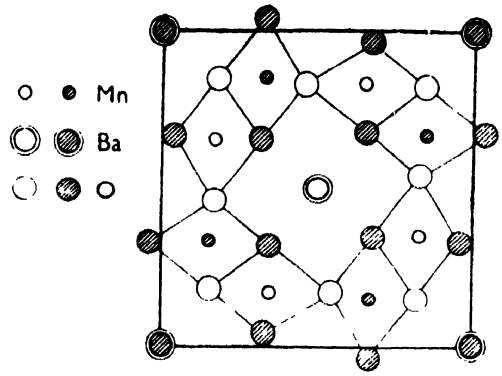



Fig. 11. Structure of Hollandite, open circles denote ions at $Z = 0$ and the filled circles at $Z = \frac{1}{2}$.

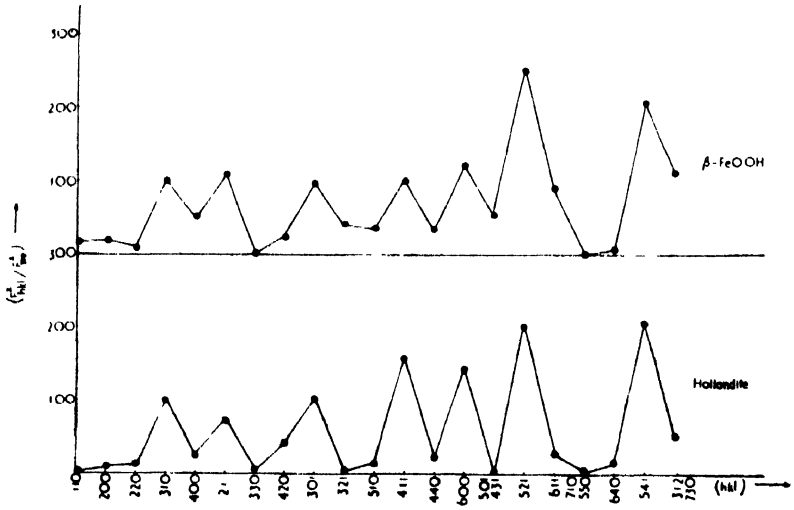



Fig. 12. Comparison of $F^2_{hkl}/F^2_{31}$ values for Hollandite and $\beta$-FeO.OH.

The diameter of the $Cl^-$ ion (3.62 A) is greater than the $c$ dimension of $\beta$-FeO.OH (3.023 $\pm$ 0.005 Å). This also suggests that Cl cannot be present in the structure stoichiometrically. The reason that $\beta$-FeO.OH could not be prepared from any ferric salt containing Br ions can be explained by the fact that the diameter of $Br^-$ ion (3.90 Å) is too big for being placed along the $c$ axis of $\beta$-FeO.OH. Moreover, the similarity between the curves for $F^2_{hkl}/F^2_{310}$ ratio of Hollandite (calculated) and $\beta$-FeO.OH (observed), as shown in Fig. 12, also suggests a similarity between the two structures.

## DISCUSSION

From the present study of iron oxides and hydroxides it seems quite evident that there are two definite series. The starting point of one series is the white $Fe(OH)_2$ and the basic ferrous salts, prepared by adding insufficient alkali, give rise to the other series. Most of the oxides and oxyhydroxides are the result of oxidation or dehydration of $Fe(OH)_2$. $\gamma$-FeO.OH, which could not be prepared from $Fe(OH)_2$ in any way, definitely belongs to the other series.

The formations and transformations of almost all the oxides and oxyhydroxides of iron can now be well represented by the Fig. 13. It is quite certain that all of them except $\beta$-FeO.OH are built up of close-packed oxygen layers and the nature of packing depends upon the structures of the individual phases. Fig. 13 shows the different form of transformations from one phase to another. As has been described in earlier chapters, the nature of all these transformations suggest that they take place, not by the complete breakdown of the structures of the origin phases but by simple shifting and re-stacking the different layers in the original structures. These observations naturally support the idea that whenever the steric conditions permit, solid state transformation, even if a large amount of the material is lost from the system, can proceed by a minimum rearrangement of the structures of the single crystals, involving little more than the mechanisms of dislocation glides, such as producing stacking faults and twinning.

The most interesting feature of the different members of the iron oxides and hydroxides groups is that most of them are built up of hexagonal close-packed or cubic close-packed layers of oxygen and hydroxyl ions. The sequences of the layers may be represented by ABABAB...or ABCABCABC... respectively. In some cases, some slight variations in the stacking of layers other than the conventional ones are possible.

$Fe(OH)_2$ is built up of hexagonal close-packed layers, the sequence of the layers being AcB-AcB, where the capital letters denote the positions of the anions and the small letters denote the position of the cation. When it changes into $\delta$-FeO.OH, on oxidation by strong oxident, there is no substantial change in the arrangement of layers. As it can be seen from the proposed structure for $\delta$-

FeO.OH, the arrangement of layers is the same as that of $Fe(OH)_2$. The difference in the two structures is that in $\delta$-FeO.OH the one H ion must leave the lattice and

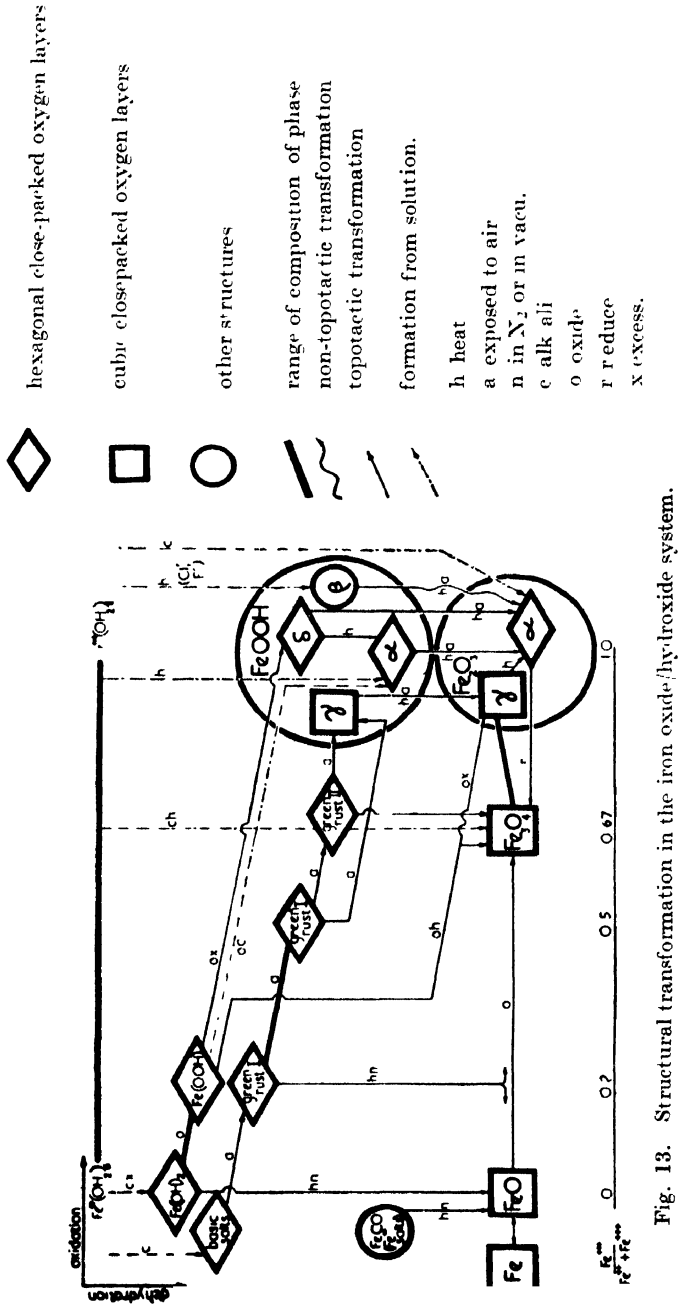



Fig. 13. Structural transformation in the iron oxide/hydroxide system.

the iron ion is divided into two parts so that the two octahedral positions between the oxygen and hydroxyl layers may be occupied. Thus, from the sequence AcB-AcB in $Fe(OH)_2$ it changes into $A\frac{1}{2}cB\frac{1}{2}cA\ldots$ in $\delta$-FeO.OH. Again, in the transformation of $Fe(OH)_2 \rightarrow FeO$, it can be seen that the two hydroxyl layers in the former give up hydrogen in the form of water and form a single layer of oxygen in FeO. Here the hexagonal close-packed layers in $Fe(OH)_2$ transform into cubic close-packed layers in FeO, the original [001] axis of $Fe(OH)_2$ becoming the [111] axis of FeO. The transformation of $FeO \rightarrow Fe_3O_4$ can also be explained in terms of topotaxy. The addition of extra oxygen to FeO does not make any substantial change in the original structure so far as the stacking of the oxygen layers except changing the axial lengths (the axial lengths of $Fe_3O_4$ are nearly double those of FeO). The directions of the principal axes remain the same after transformation into $Fe_3O_4$. Though all the transformations such as $Fe(OH)_2 \rightarrow \delta$-FeO.OH, $Fe(OH)_2 \rightarrow$ FeO and $FeO \rightarrow Fe_3O_4$ can be explained in terms of topotaxy, it is not yet known how $Fe(OH)_2$ can convert directly into $Fe_3O_4$ on oxidation. If FeO were found in between $Fe(OH)_2$ and $Fe_3O_4$, then it would have been possible to describe the whole transformation as topotactic.

That two topotactic transformations can take place one after another was clearly illustrated by the transformation of a single crystal of Lepidocrocite ($\gamma$-FeO.OH) into Maghemite ($\gamma$-$Fe_2O_3$) and then into Hematite ($\alpha$-$Fe_2O_3$). Lepidocrocite is built up of nearly cubic close-packed oxygen-hydroxyl layers, but their cubic faces are arranged at approximately 45° to the *c*-axis. When it is heated, one of the two adjoining hydroxyl layers is removed as water, converting the two layers into a single layer of oxygen only. The whole arrangement of the atoms then corresponds to a spinel structure (maghemite) having an oriented relationship with the original structure. When this transformed crystal is heated further, further change takes place. On the (111) faces of the freshly prepared Maghemite (transformed from $\gamma$-FeO.OH) the Hematite crystals grow up beautifully. Here, the [111] axis of the Maghemite becomes the [001] axis of the hematite crystals. The sequence of the oxygen layers is ABCABC in $\gamma$-$Fe_2O_3$, and ABABAB in $\alpha$-$Fe_2O_3$, maghemite being cubic and hematite rhombohedral. There is also another interesting point to note in this transformation. In the X-ray photographs, the spots due to Maghemite are diffuse, whereas the spots due to Hematite are fairly sharp. The diffuseness of the maghemite spots indicates the change from an asymmetrical arrangement of the oxy-hydroxyl layers in $\gamma$-FeO.OH to a more symmetrical arrangement of oxygen layers in $\gamma$-$Fe_2O_3$. The more exact fit between Maghemite and Hematite, which permits easy recrystallisation, accounts for the sharpness of the Hematite spots. The Maghemite-Hematite transformation is very close to that which occurs in the Magnetite-Ilmenite transformation found in natural minerals. Here the original titaniferrous Magnetite breaks down into Ilmenite ($FeTiO_3$), the structure of which is similar to that of Hematite ($\alpha$-$Fe_2O_3$).

As in the former transformation, here also the *c*-axis of Ilmenite becomes parallel to the [111] axis of Magnetite.

Some irregular arrangements of the oxy-hydroxyl layers other than the conventional ones, can be seen in the green rust I and II. In green rust I the arrangement of the layers is AB'CBC'ACA'B, whereas in II it is like A'BACA'BAC. Both these green rusts contain blocks of cubic and hexagonal close-packed layers. The cubic and hexagonal portions are ABC and BCB respectively in green rust I and BAC and ABA respectively in green rust II. Though the transformation of these two green rusts into $\mu$-$\gamma$-FeO.OH or to FeO could not be demonstrated using single crystals, it appears that both the transformations are topotactic. Indirect evidence that the change is topotatic is provided by the fact that the green rusts I and II always give rise to cubic close-packed oxides or hydroxides. It can be seen that by suppressing one layer in three of the green rust I and one layer in every four in green rust II, as shown by the dashed letters, both the rusts transform into cubic close-packed structures, with the stacking of layers as ACBACB...and BACBAC... in green rust I and II respectively, whereas the direct oxidation of the hexagonal close-packed $Fe(OH)_2$ leads to two hexagonal close-packed oxyhydroxides, depending upon the nature and rate of oxidation.

A topotactic change involving the loss of atoms at one state and a gain of atoms at the next stage is also clearly illustrated in the transformation of $FeCO_3 \rightarrow FeO \rightarrow Fe_3O_4$. In the first stage $CO_2$ leaves the original structure; in the second stage oxygen enters into the lattice. This removal and the addition of atoms did not prevent a topotactic transformation.

It is now clear that most of the reactions shown in Fig. 13 can be expected to take place with oriented relationships between the original and the transformed phases. The exception is $\beta$-FeO.OH$\rightarrow\alpha$-$Fe_2O_3$. There is no similarity between the structures of $\beta$-FeO.OH and $\alpha$-$Fe_2O_3$; on dehydration, the structure of $\beta$-FeO.OH breaks down completely and renucleation is needed for the transformation process.

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